Electro-diffusion phenomena in C_{60} thin films

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As part of our ongoing research program to produce semiconductor devices based on the C_{60} thin films, we report here on our first attempts at the intercalative doping of C_{60} thin films by diffusion of metals. Two techniques were employed: (a) chemically-induced counter electro-diffusion of Cu and I_2 into a C_{60} matrix; (b) diffusion of Au under the action of an external electric field.

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The most commonly practiced kind of doping of a C_{60} solid is intercalation whereby dopants are located between the C_{60} molecules in the interstitial positions of the host crystal structure [1]. Intercalated fullerides may be produced by the simultaneous vacuum evaporation of C_{60} molecules and dopant atoms or by diffusion of dopant atoms into pristine C_{60} crystal. Such diffusion may occur as a spontaneous process or it can be induced by an external stimulus, like vapor pressure or an electric field applied to the sample. Study of an impurity diffusion in C_{60} crystals and thin films has recently become one of the important subjects in fullerene research [2].

This paper presents the results of an experimental study of two diffusion phenomena in C_{60} thin films (with emphasis on the possibility of semiconductor doping of the material): (a) chemically-induced counter electro-diffusion (CICED) of Cu and I_2 into a C_{60} matrix, (b) diffusion of Au under the action of an external electric field. The resulting samples were characterized by X-ray diffraction, Auger Electron Spectroscopy (AES), and conductivity measurements.

1. Experimental

C_{60} films of 100 nm thickness were grown, using a vacuum deposition technique, on glass and mica substrates as well as on glass substrates predeposited with a Cu sublayer [3,4].

The crystalline structure of these C_{60} films was studied by X-ray diffraction (XRD). The morphology of the front surface of the films, in particular grain sizes at the front surface was studied by Atomic Force Microscopy.

Elemental composition at the surface and in-depth concentration distributions ("sputter depth-profiling") for C_{60} films were studied by AES combined with controlled Ar ion bombardment. The details of the AES measurements are given elsewhere [5].

Conductivity of the C_{60} films was measured in two- and four-probe configurations of electrodes (Fig. 1), using a Hewlett Packard 4140B pico-meter/dc voltage source.

The other experimental details will be given below.

2. Results and discussion

2.1. CICED of Cu and I_2 into the C_{60} matrix. Recently [5] we developed a new technique for doping (intercalation) of C_{60} thin films, so-called CICED. The technique involves the vacuum deposition of highly crystalline C_{60} thin film onto a metal (Cu or Au, or Ag) sub-layer [3] and subsequent exposure of the samples to a reactive gas atmosphere.

If oxygen is employed as the reactive gas atmosphere, a diffusion of oxygen atoms through the front surface of the fullerene film is observed and a corresponding slow counter diffusion of metal from the sub-layer occurs (with a characteristic time measured in months). Analysis of the resulting doped material after 10 months of air-exposure of the Cu-supported C_{60} films, at room-temperature, revealed the presence of Cu and O atoms at all depths over the samples and the formation of a complex which we referred to as $Cu_xO_yC_{60}$. We have published elsewhere [5] the detailed results of the oxygen-induced doping experiment together with a suggestion that the following CICED multi-step process takes place under the experimental conditions. 1) Well-known diffusion of molecular oxygen (O_2) from air into the C_{60} film. 2) Emission of free electrons from the Cu sub-layer to oxygen molecules in the C_{60} matrix. 3) Generation of an internal electric field between $(O_2–C_{60})^-$ complexes and the Cu^+ sub-layer. 4) Drift of Cu^+ from the sub-layer to the $(O_2-C_{60})^-$ complexes. 5) Formation of the $Cu_xO_yC_{60}$ complex.

In the case of an iodine atmosphere, the metal diffusion was observed to occur on a time scale which is orders of magnitude faster. Indeed, even 10 minutes of exposure in

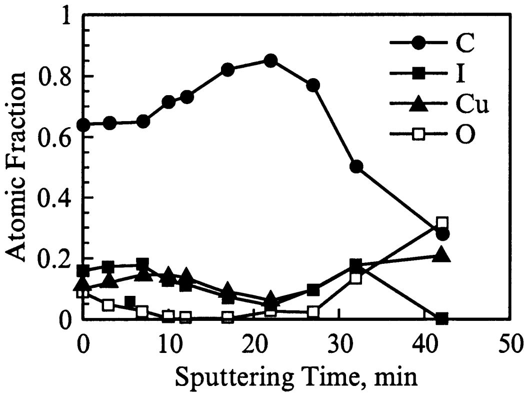

Figure 1. Depth distribution of Cu, I, O and C atomic fractions (in units corresponding to the time of sputtering by Ar ions), measured by AES, after 10 minutes of exposure in an I_2 atmosphere of a Cu-supported C_{60} film.

an I_2 atmosphere, of the Cu-supported C_{60} films, at room-temperature, led to a complete disappearance of the Cu sublayer due to Cu diffusion into the C_{60} film. X-ray diffraction (not shown) revealed an absence of any Cu peaks. At the same time, together with the $\{111\}$-reflections from C_{60} lattice, four intense CuI peaks appeared after exposure. AES depth profiling measurements of this sample (Fig. 1) revealed the presence of Cu and I_2 at all depths over the C_{60} film (the most surprising result being that Cu is present even at the front surface of the film!). A clear correlation between the Cu and I atomic fractions is also in evidence. This indicates the existence of CuI over the entire thickness of the C_{60} film. In other words, we may conclude that the exposure of a Cu-supported C_{60} film to an I_2 atmosphere leads to counter diffusion of Cu and I_2 into the C_{60} matrix resulting in the formation of a C_{60}–CuI composite material.

Using a two-probe measuring technique, a substantial increase in the dark conductivity (from 10^{-9}–$10^{-12}\,(\Omega\cdot\mathrm{cm})^{-1}$ to 10^{-3}–$10^{-4}\,(\Omega\cdot\mathrm{cm})^{-1}$) was observed after CuI doping. Unfortunately, no semiconductor behavior and photo-conductivity of the doped samples were observed. These results suggest electronic transport occurs mainly by the percolation through the CuI phase of the composite material which has low dark resistivity but it is no photosensitive.

We believe however, that by using this ”counter diffusion” approach and optimizing the process conditions, it is possible to produce C_{60}-based materials doped with various compounds in the form of both phase-separated composites and solid solutions (intercalated fullerides). Intercaltion of C_{60} with compounds is now becoming a research direction of vital importance because of the following findings published very recently. Schon et al. [6] discovered superconductivity with a transition temperature $T_c = 52$ K in a single crystal of C_{60} doped by holes using the technique of gate-induced doping in a field-effect transistor. This value of T_c is the highest ever observed in a C_{60}-based material. Furthermore, the authors believe that T_c's up to 100 K should be achievable in a suitably expanded, acceptor-intercalated C_{60} lattice. On the other hand, to the best of our knowledge, the only successful examples of the doping of C_{60} by acceptors is intercalation by compounds such as $InCl_3$, AsF_5, SbF_5, $SbCl_5$ [7–9].

Furthermore, the important of the presented CICED results — extremely fast metal diffusion into the C_{60} film under the action of internal electric field — suggested that one should attempt the diffusion of metals into C_{60} films under the action of an external electric bias.

2.2. Diffusion of Au into C_{60} films under the action of an external electric bias. Three types of C_{60} films grown on an insulator substrate were used in these experiments: (a) highly dispersed films (grain size of ~ 20 nm, no texture), (b) films of intermediate-crystallinity

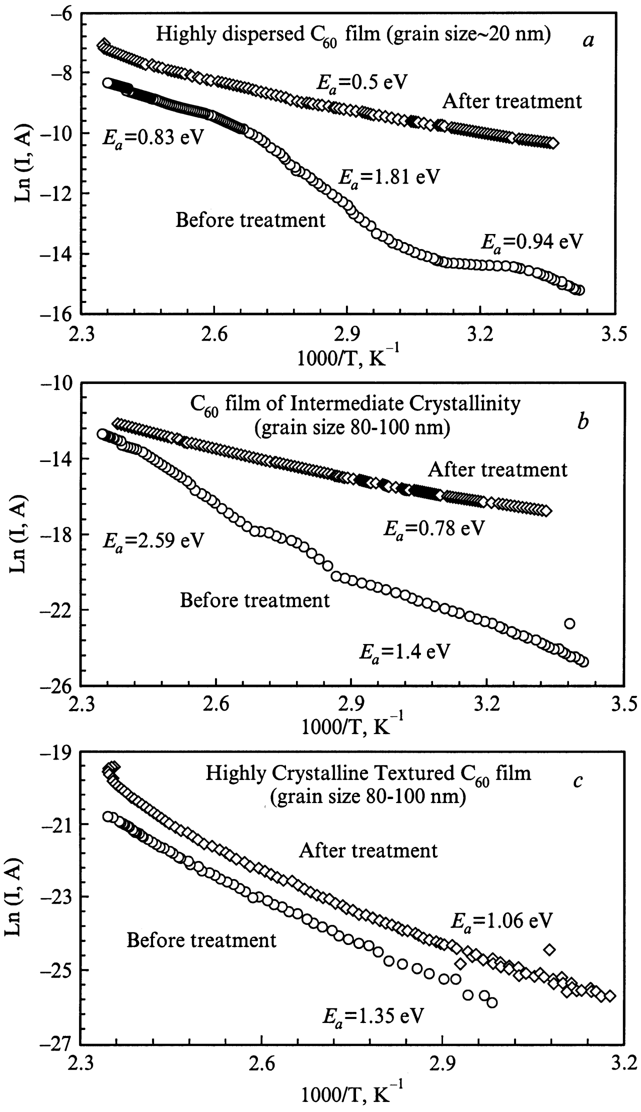

Figure 2. Temperature dependence of two-probe coplanar conductivity, before and after treatment of the C_{60} films for 1 hour under an electric field of 500 V/cm at 150°C: (*a*) a highly dispersed film, (*b*) a film of intermediate-crystallinity, (*c*) a highly crystalline film.

Correlation between the grain sizes in C_{60} films and their value of activation energy of conductivity, after treatment for 1 hour under an electric field of 500 V/cm at 150°C

C_{60} films Structure	Grain Size, nm	Activation energy, eV
Highly Dispersed	~ 20	0.5
Intermediate Crystalline	80–100	0.78
Highly Crystalline Textured	500–1500	1.06

(grain size of 80–100 nm, no texture), (c) highly crystalline films (grain size of 500–1500 nm, $\langle 111 \rangle$-texture).

The conductivity measurements were performed *in situ* while pumping the quartz tube with sample up to a dynamic vacuum of 10^{-6} Torr and heating of the samples up to elevated temperatures. After the sample temperature had reached a value of 150°C we applied a series of external electric fields, with strengths of 150, 300 and 500 V/cm, between the Au-electrodes. We observed an increase in time of the measured value of current (i. e. film conductivity) the longer the field was applied. The rate of increase was observed to be intensified as the electric field strength was increased. These results are in aggreement with those of a similar experiment performed by Firlej et al. [2,10]. However, in addition, we revealed a strong correlation between the rate of conductivity increase and the crystalline structure of the films: for an increase of the film grain sizes, the rate of conductivity increase was observed to diminish.

Fig. 2 shows the temperature dependence of the two-probe coplanar conductivity of C_{60} films with various degrees of crystallinity, before and after treatment by a 500 V/cm electric field for 1 hour at a temperature of 150°C. All temperature-dependent results show a semiconductor-like activated behavior. Furthermore, we can certainly conclude that the values of activation energy decrease as a result of treatment in all three cases. This is direct evidence that semiconductor doping was occurring during the treatment.

The other interesting feature of these results is an observed relationship between the decrease in activation energy and the crystalline structure of the samples (Table 1). Specifically, the minimum value of activation energy after the treatment (or in the other words, the maximum doping effect) was observed for those samples with the smallest grains. In this case, room-temperature conductivity was found to increase by more than 4 orders of magnitude (Fig. 2, *a*). Conversely, the maximum activation energy (i. e. the minimum doping effect) was observed for the highly crystalline sample (Fig. 2, *c*). Both decrease in activation energy and increase of conductivity values, after treatment, with decrease in grain sizes are in evidence.

The electrodiffusion experiment using a four-probe configuration of electrodes demonstrated similar results. AES and *X*-ray Photoelectron Spectroscopy (XPS) characterization of the doped samples as well as photoconductivity measurements are in progress.

In general, a diffusion rate of an impurity atom is known to be higher along grain boundaries than within a crystal grain [11]. We interpret the observed doping behavior as the electrodiffusion of Au from an electrode, dominantly along grain boundary, and the subsequent intercalation of the C_{60} lattice by Au atoms.

1) Structural and chemical changes in Cu-supported C_{60} thin films during their room–temperature–exposure to I_2 atmosphere were studied by XRD, AES, XPS and conductivity measurements. A C_{60}–CuI composite material was found to be produced during the exposure of Cu-supported C_{60} film to an I_2 atmosphere. Even 10 minutes of exposure resulted in complete disappearance of the Cu sub-layer and the formation of a CuI phase over the whole thickness of the C_{60} film. The room temperature dark conductivity of the CuI-doped samples was observed to have increased by several orders of magnitude but the semiconductor behavior was not in evidence.

2) We report the effect of an external electric field of the *in situ* measured conductivity of C_{60} films with different degrees of crystallinity. Semiconductor behavior with increased conductivity values (by orders of magnitude) and decreased cunductivity activation energy has been demonstrated for the doped samples. The results are explained by electrodiffusion of Au from an electrode, dominantly along grain boundaries, and the subsequent intercalation of C_{60} lattice by Au atoms.

References

[1] M.S. Dresselahaus, G. Dresselahaus, P.C. Eklund. Science of Fullerenes and Carbon Nanotubes. Academic Press, San Diego etc. (1996).

[2] L. Firlej. Condensed Matter News **8**, 22 (2000).

[3] E.A. Katz. US Patent N 5 876 790, 2 March (1999).

[4] E.A. Katz, D. Faiman, S. Shtutina, A. Isakina. Thin Solid Films **368**, 49 (2000).

[5] E.A. Katz, D. Faiman, S. Shtutina, N. Froumin, M. Polak, A.P. Isakina, K.A. Yagotintsev, M.A. Strzhemechny, Y.M. Strzhemechny, V.V. Zaitsev, S.A. Schwarz. Physica **B304**, 348 (2001).

[6] J.H. Schön, C.H. Kloc, B. Batlogg. Nature **408**, 549 (2000).

[7] W. Maser, S. Roth, J. Anders, J. Reichenbach, M. Kaiser, H. Byrny, H. Schier, M. Filzmoser. Synth. Metals **51**, 103 (1992).

[8] W.R. Datars, T.R. Chien, R.K. Nkum, P.K. Ummat. Phys. Rev. **B50**, 4 937 (1994).

[9] M. Barati, P.K. Ummat, W.R. Datars. Solid State Commun., **106**, 91 (1998).

[10] L. Firlej, N. Kirova, A. Zahab. Phys. Rev. **B59**, 16 028 (1999).

[11] J.C. Fisher. J. Appl. Phys., **22**, 74 (1951).